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Impact of molecular quadrupole moments on the energy levels at organic heterojunctions

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The functionality of organic semiconductor devices crucially depends on molecular energies, namely the ionisation energy and the electron affinity. Ionisation energy and electron affinity values of thin films are, however, sensitive to film morphology and composition, making their prediction challenging. In a combined experimental and simulation study on zincphthalocyanine and its fluorinated derivatives, we show that changes in ionisation energy as a function of molecular orientation in neat films or mixing ratio in blends are proportional to the molecular quadrupole component along the π - π -stacking direction. We apply these findings to organic solar cells and demonstrate how the electrostatic interactions can be tuned to optimise the energy of the charge-transfer state at the donor–acceptor interface and the dissociation barrier for free charge carrier generation. The confirmation of the correlation between interfacial energies and quadrupole moments for other materials indicates its relevance for small molecules and polymers.

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Organic semiconductors gained much attention because of their attractive application in low-cost, large area, and flexible electronic devices^{1–4}. While organic light-emitting diodes (OLEDs) already entered the market in thin film displays, several other promising applications such as solar cells, transistors, photodetectors, or lasers still require improvements in performance. In contrast to their inorganic counterparts, organic semiconductors typically consist of weakly bound molecules, where charge carriers occupy rather localised states. Associated to these states are the ionisation energy (IE) and electron affinity (EA) of organic molecules, which are related to the transport energies of holes and electrons and, consequently, determine the functionality of electronic devices^{5,6}.

In organic solar cells (OSCs), fundamental processes determining the device performance are the dissociation of charge-transfer (CT) states at the donor–acceptor interface into free charges and their non-geminate recombination via CT states back to the ground state^{7–9}. Therefore, the CT state energy (E_{CT}) determines the open-circuit voltage (V_{oc}) of OSCs¹⁰, while its difference to the energy of separated charges (E_{CS}) influences the generation efficiency of free charge carriers and, thus, crucially affects both the short-circuit current density (j_{sc}) and the fill-factor (FF)^{11,12}. Both E_{CT} and E_{CS} are linked to IE of the donor and EA of the acceptor.

IE and EA of molecules in organic films significantly depend on molecular orientation and mixing ratio in blends^{13–15}. In particular, charge–quadrupole interaction can induce large electrostatic shifts of the electronic levels in crystalline films^{16–19}, which, for example, allows in blends with molecular intermixing, a continuous tuning of IE and EA by adjusting the ratio of two different molecular species^{20,21}. Furthermore, simulations indicated that these interactions can assist the dissociation of CT states at planar donor–acceptor interfaces^{22,23}. However, it remains an open question to which extent such findings for these model systems are general and, particularly, how they are applicable to donor:acceptor blends without long-range order which are usually employed in efficient OSCs.

In this study, we demonstrate the tunability of the solid-state IE by charge–quadrupole interactions and their relevance in systems with long-range and short-range order, being, thus, relevant for most organic devices. As a model system, we choose zincphthalocyanine (ZnPc) because of the possibility to gradually change its quadrupole moment (QPM) by stepwise fluorination (F_n ZnPc)²⁰. In order to establish the role of the quadrupole component perpendicular to the molecular plane (Q_π), we measure for F_n ZnPc the change in IE with molecular orientation, film thickness, and mixing ratio in blends. The ultraviolet photoelectron spectroscopy (UPS) analysis reveals a linear change of IE with Q_π in all cases. Moreover, when applying these findings to OSCs, we demonstrate how QPMs influence E_{CT} at planar and bulk heterojunctions between donor and acceptor. Time-delayed collection field (TDCF) measurements further show that electrostatic gradients induced by QPMs can assist free charge carrier generation in these solar cells. Finally, we extend the study to other material systems, indicating the relevance of the findings for a large variety of organic semiconductors.

Results

Dependence of thin film energies on the component Q_π . IE and EA of molecules in thin films deviate from their gas-phase values, IE_0 and EA_0 , due to polarisation effects^{24–26}. In weakly bound solids with localised states, the electrostatic corrections (Δ_+ and Δ_-) to the gas-phase values consist of an induced and a permanent contribution. While the first term decreases the distance between IE and EA, the latter originates from the interaction of

excess charges with static charge distributions and shifts IE and EA equally^{17–20}. We concentrate on the permanent contribution in this study, which is often dominated by the charge–quadrupole term in the multipole expansion because molecules with dipole moments often stack with alternating molecular orientations in ordered organic solids^{16,18}. In this case, the permanent contribution can be approximated by a sum over the interaction energies of a charged molecule, described by its atomic excess charges q_j at positions \mathbf{r}_j , with the quadrupole tensors \mathbf{Q}_i of all surrounding molecules at sites \mathbf{r}_i ²⁷:

$$E_Q = \sum_{ij} \frac{q_j}{8\pi\epsilon_0\epsilon_r} \cdot \frac{(\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{Q}_i \cdot (\mathbf{r}_i - \mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|^5}, \quad (1)$$

where we use the dielectric permittivity ϵ_r as a macroscopic constant. We describe the charged molecule by its actual distribution of atomic charges to have an appropriate description at distances in the range or below the spatial extent of molecules.

Due to the strong dependence of E_Q on distance, E_Q changes with the chemical and crystal structure of the compound. Like many other planar molecules, F_n ZnPc typically arranges in a π – π -stacking geometry^{28,29}, where the intermolecular distance along the stacking direction (approximately 3.8 Å²⁸) is significantly smaller than along the other two directions (13–14.5 Å³⁰). Therefore, we first investigate if the quadrupole component perpendicular to the molecular plane (Q_π) dominates E_Q (see Fig. 1 for Q_π values) by analysing for F_n ZnPc layers (20 nm) the difference in IE between face-on and edge-on orientation of the molecules (Fig. 2a, see Supplementary Figs. 1–3 and Supplementary Note 1 for X-ray scattering results). The representative UPS spectra in Fig. 2b show that IE of a ZnPc film in edge-on orientation is 0.22 eV smaller as compared to the film in face-on orientation, in agreement with previous results¹³. In contrast, F_8 ZnPc exhibits an IE value in edge-on orientation that is 0.37 eV larger than the IE value in face-on orientation. To connect this behaviour to molecular properties, we calculate Q_π by density functional theory (DFT) for ZnPc and its fluorinated derivatives (results in Supplementary Table 1). As displayed in Fig. 2c, the difference in IE between edge-on and face-on orientation increases with Q_π from ZnPc to F_{16} ZnPc.

To prove that Q_π dominates in E_Q (see Eq. 1), we calculate E_Q for a single charged molecule at the film surface for both orientations (see Methods and Supplementary Fig. 4). The difference in E_Q between both orientations exhibits the same correlation with Q_π as observed for the IE difference in experiment (Fig. 2c). Interestingly, the simulations reveal that the relevant range of charge–quadrupole interactions is different between both molecular orientations (Supplementary Fig. 5). For edge-on orientation, E_Q is dominated by interactions between the next few neighbours along the π – π -stacking geometry. For face-on orientation, E_Q is also dominated by interactions with Q_π components at small integration limits, which however is compensated by the interaction with other components when the integration limit in the lateral direction becomes larger than 100 nm. Previous investigations indicate that the interaction with other components than Q_π can be even more dominant in face-on orientation for molecules with a different symmetry than F_n ZnPc such as pentacene, having two molecular short axes^{19,31}. In the absence of long-range order, such as in donor:acceptor blends with crystal sizes much smaller than 100 nm, the interaction of charges with Q_π components should dominate^{32–34}.

To further verify the dominance of charge–quadrupole interactions along the π – π -stacking direction for edge-on orientation, we measure IE of F_n ZnPc for coverages below the monolayer thickness and evaporate the material stepwise onto

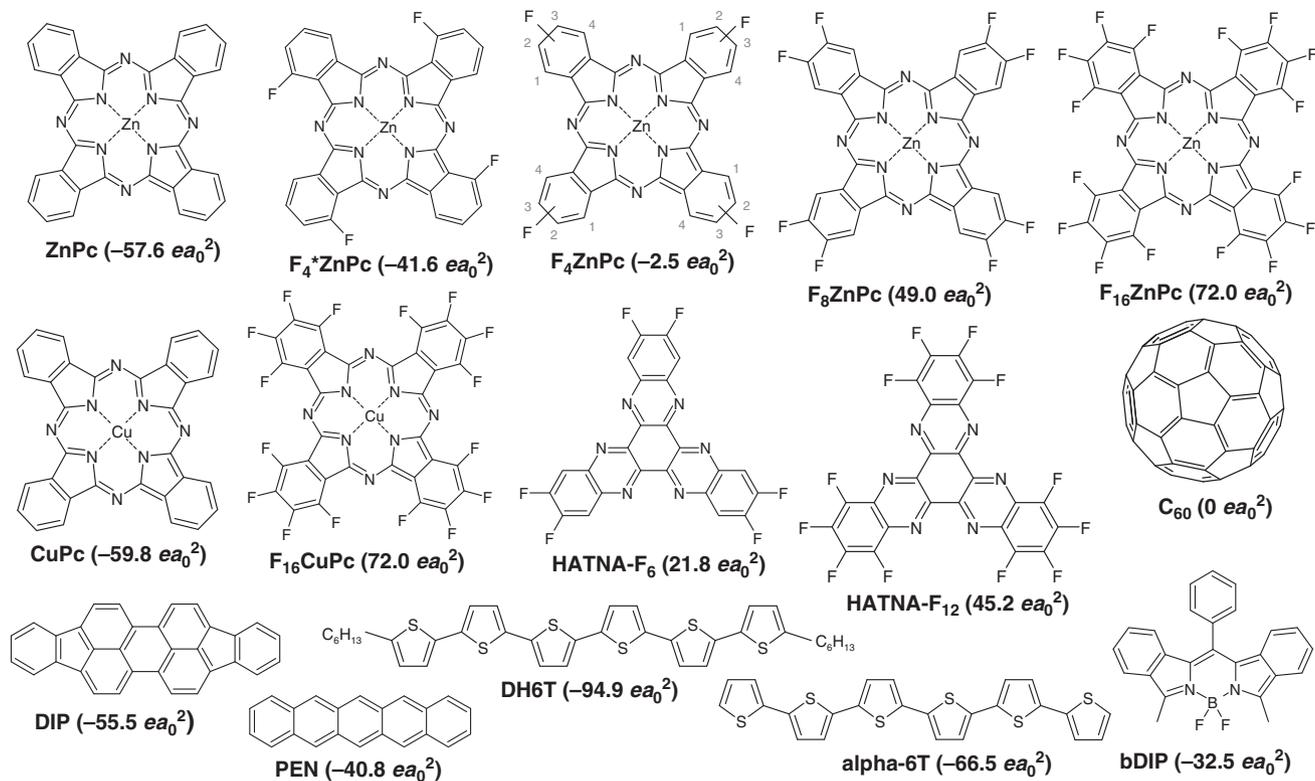


Fig. 1 Chemical structures and quadrupole components of small molecules: Values in brackets are the quadrupole components perpendicular to the molecular plane (Q_{π}), as calculated with density functional theory (DFT). Supplementary Table 1 summarises the in-plane quadrupole components. F_4ZnPc is a mixture of different isomers, where the fluorine atom is bonded to one of the two outer carbon positions (2 or 3)²⁰

p-doped BPAPF, leading to an edge-on orientation in thin films (Supplementary Figure 6). IE at very small coverages, denoted as IE_s , deviates strongly from the value of thick layers (see dotted lines in Fig. 2d). Notably, for all ZnPc derivatives, IE_s is reduced by 0.6 eV compared to their respective gas-phase ionisation energies IE_0 , indicating minor influence of charge–quadrupole interactions on IE at low coverages. With increasing layer thickness, IE strongly changes and approaches the value of a thick edge-on oriented film when the monolayer thickness (13–14.5 Å³⁰) is reached. The strong IE shift can be explained by the formation of an ordered monolayer in edge-on orientation, leading to an increase of the magnitude of E_Q due to charge–quadrupole interactions along the π – π -stacking direction. In good agreement, the change of IE scales with the Q_{π} value of the respective ZnPc derivative (Supplementary Fig. 6c). Note that the change in IE until the first edge-on monolayer is formed can occur for different growth modes, such as island growth or transition of molecular orientation from face-on to edge-on.

After having demonstrated the strong effect of Q_{π} on the energy levels in model systems based on ZnPc derivatives, we further analyse its impact in donor:acceptor blends which are typically used in OSCs. Such blended structures usually exhibit significant structural disorder and phase separation that both can change with mixing ratio^{13,32,35,36}. Previous studies found changes of energy levels with donor:acceptor mixing ratio, which were assigned to changes in crystal size and to electrostatic changes^{13,15,37}. We trace back these energetic changes to the influence of the molecular tuning parameter Q_{π} .

We measure the energy levels of $F_8ZnPc:C_{60}$ blends at different mixing ratios (see UPS spectra in Supplementary Fig. 7). As shown in Fig. 3a, IE of F_8ZnPc decreases by more than 300 meV with increasing C_{60} content. IE of C_{60} shows a similar change, which suggests that a large amount of donor and

acceptor molecules interact electrostatically with the other species despite the phase separation in these blends. The larger IE change of F_8ZnPc at higher C_{60} contents indicates that F_8ZnPc molecules which are closer to C_{60} molecules experience a larger electrostatic shift.

To validate that the electrostatic changes originate from charge–quadrupole interactions, we compare the behaviour of $F_8ZnPc:C_{60}$ blends to previously reported ZnPc: C_{60} blends¹³, as ZnPc and F_8ZnPc exhibit a similar magnitude but a different sign of Q_{π} . Figure 3b shows the electrostatic correction Δ_+ of IE for ZnPc and F_8ZnPc blended with C_{60} . While Δ_+ differs strongly between ZnPc and F_8ZnPc in pure layers, this difference reduces continuously with increasing C_{60} concentration, and Δ_+ finally approaches -0.6 eV. This value is also observed for very small coverages of (F_8)ZnPc, indicating that the charge–quadrupole interaction energy E_Q approaches 0 for high C_{60} contents (see Fig. 2d for comparison). Therefore, we attribute the decrease (increase) of IE of F_8ZnPc (ZnPc) with increasing C_{60} content to the interaction of charges with a reduced number of Q_{π} components of the donor.

The dominance of charge–quadrupole interactions along the π – π -stacking direction is attributed to the shorter intermolecular distance in this direction for the ZnPc derivatives. To verify whether this simple model is also valid for other materials, we extend our investigation to other molecules that show a strong dependence of IE on molecular orientation in neat films^{13,14,38–41} or on mixing ratio in donor:acceptor blends^{15,37} (see Fig. 1 for chemical structures). We calculate their QPMs and observe that for both cases the change in IE scales linearly with the respective Q_{π} (Supplementary Fig. 8). Notably, the slope is surprisingly similar to the one observed for intermixed blends of different ZnPc derivatives²⁰ (Supplementary Fig. 9). Charge–quadrupole interactions are also relevant for polymers. Similar to

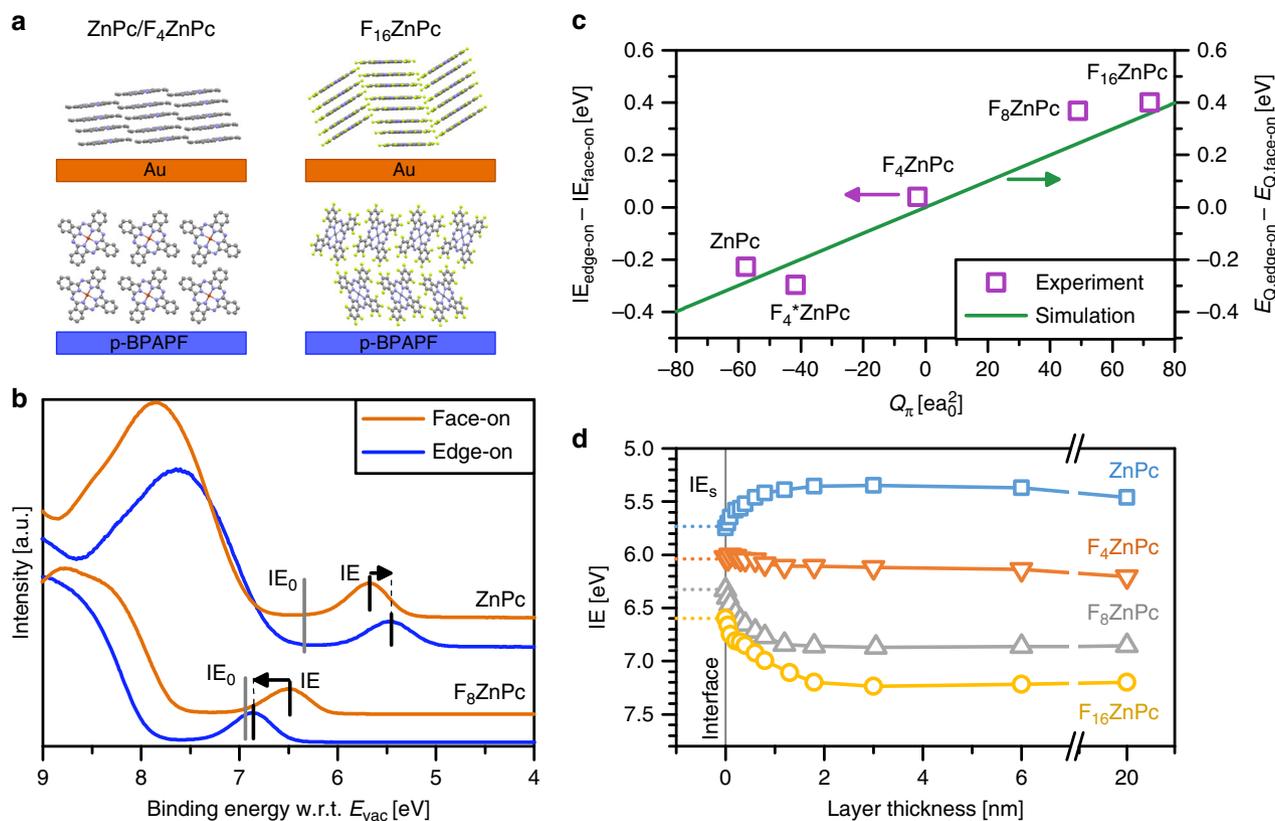


Fig. 2 Dependence of IE on charge–quadrupole interactions along the π – π -stacking geometry: **a** Sketch of the film structure of ZnPc, F₄ZnPc and F₁₆ZnPc, showing the difference in molecular orientation between two different substrates. **b** UPS spectra of thin films of ZnPc (top) and F₈ZnPc (bottom) in edge-on orientation (substrate: p-doped BPAPF on silver) and face-on orientation (substrate: gold). The different quadrupole moments of ZnPc and F₈ZnPc cause electrostatic shifts in opposite directions from the gas-phase IE (IE_0 , obtained with DFT) to the IE value of thin films (obtained with UPS). **c** The difference in IE between edge-on and face-on orientation in UPS experiments (violet squares) scales with the calculated quadrupole component perpendicular to the molecular plane (Q_{π}). The green solid line shows the difference in the charge–quadrupole interaction energy E_Q between both orientations, as obtained from simulation. **d** IE of F_nZnPc on p-doped BPAPF, obtained by subtracting the substrate spectrum from the superimposed spectra (see Supplementary Fig. 6a), changes strongly during the formation of the first monolayer in edge-on orientation due to charge–quadrupole interactions along the π – π -stacking direction. The slight changes of IE from 3 to 20 nm are also observed in simulation and can be explained by increased interactions with other quadrupole components than Q_{π} . IE_s (dotted lines) is attributed to molecules with $E_Q \approx 0$, being 0.6 eV smaller than IE_0 .

sexithiophene (alpha-6T), poly-3-hexylthiophene (P3HT) shows a smaller IE for end-on orientation with the polymer chain perpendicular to the substrate plane⁴². This analysis indicates that the impact of Q_{π} on thin film energy levels is relevant for many organic materials including varying molecular structures and different morphologies of their (blend) films.

Impact of Q_{π} at donor–acceptor interfaces in solar cells. The functionality of OSCs is linked to the formation of charge-transfer (CT) states of a donor cation and an acceptor anion at their interface (Fig. 4a), mediating charge carrier dissociation and recombination in OSCs^{7,8}. In the following, we demonstrate how molecular quadrupole moments can influence the CT state energy (E_{CT}) as well as its difference to the energy of separated charges (E_{CS}). For this purpose, we analyse ZnPc:F₄ZnPc:C₆₀ solar cells based on bulk heterojunctions (BHJ) with two electron donating molecules (ZnPc and F₄ZnPc) and one acceptor (C₆₀) with a fixed volume content of the acceptor (60%). Different mixing ratios between ZnPc and F₄ZnPc are used to selectively change the average of the molecular parameters in the donor phase.

For analysing E_{CT} , we obtain the relevant gas-phase energy levels of donor and acceptor molecules ($IE_{0,D}$ and $EA_{0,A}$) as well as the intramolecular relaxation energies of their ions by DFT.

We further calculate for ZnPc/C₆₀ and F₄ZnPc/C₆₀ the Coulomb binding energies of the energetically relaxed ion pairs and find that they differ up to several 10 meV between ZnPc and F₄ZnPc because of their different charge distributions⁴³ (see Methods section and Supplementary Fig. 10a). We calculate from these parameters the expected variation of E_{CT} from ZnPc:C₆₀ to F₄ZnPc:C₆₀ (dashed line in Fig. 4b and Supplementary Fig. 10b). Experimental values of E_{CT} obtained from Gaussian fits to sensitively measured external quantum efficiency (see Supplementary Fig. 11) and electroluminescence spectra⁴⁴. In good agreement with the calculations, the experimental values increase with F₄ZnPc content (purple squares in Fig. 4b). However, the measured shift of E_{CT} is 0.1 eV larger than expected from the variation of molecular parameters, which can be partly attributed to the larger static energetic disorder at high ZnPc contents, reducing E_{CT} (Supplementary Fig. 12). In addition to energetic disorder, charge–quadrupole interactions lower the effective IE of the donor and further reduce E_{CT} at large amounts of ZnPc.

To verify the impact of charge–quadrupole interactions on E_{CT} , we additionally fabricate solar cells with a planar heterojunction (PHJ) between a ZnPc:F₄ZnPc blend layer with varying mixing ratio and a neat C₆₀ layer. The ZnPc:F₄ZnPc layer is grown on p-doped BPAPF to ensure edge-on orientation of the donor molecules, causing a large change of IE induced by

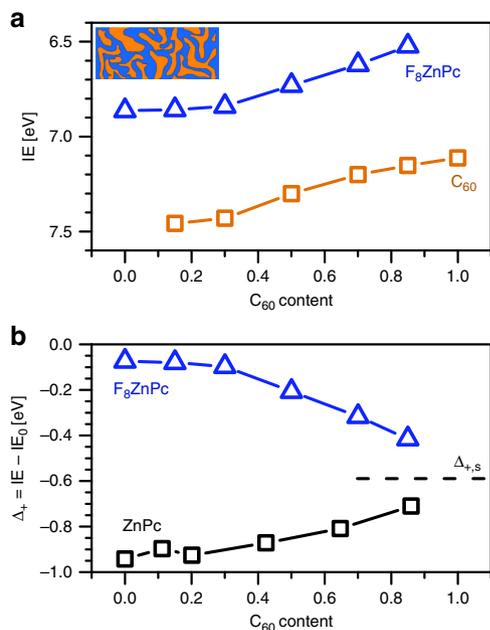


Fig. 3 Electronic levels in donor:acceptor blends: **a** IE of F₈ZnPc and C₆₀ at different molar contents of C₆₀, as obtained by UPS. **b** With increasing C₆₀ content, the electrostatic corrections Δ₊ of ZnPc and F₈ZnPc, being the difference in IE between the thin film and the gas-phase, shift towards -0.6 eV. This value is expected for negligible charge-quadrupole interaction energy (see results in Fig. 2d for very small film coverages). Experimental IE values of ZnPc:C₆₀ blends are taken from the study by Tietze et al.¹³

charge-quadrupole interactions (see Fig. 2b and Supplementary Fig. 9). At high ZnPc contents, the planar devices exhibit a significantly lower E_{CT} (green circles in Fig. 4b) than the ternary BHJ devices. This can be explained by extended long-range order, which increases the charge-quadrupole interaction energy and reduces IE of the donor for large ZnPc contents. The change of E_{CT} with donor mixing ratio directly influences V_{oc} because charge carriers recombine via CT states at open-circuit⁹. Therefore, the different shifts of E_{CT} in BHJ and PHJ devices upon changing the donor content is reflected in a similar difference in V_{oc} shift, demonstrating the relevance of charge-quadrupole interactions for important device parameters (Fig. 4c).

The generation efficiency of photocurrent depends on the dissociation barrier of CT excitons (ΔE_{diss}), which depends on the difference between E_{CS} and E_{CT} ¹¹. We next discuss how quadrupole moments can induce electrostatic gradients at the donor-acceptor interface that lead to a lower ΔE_{diss} . In the case of a negative quadrupole component $Q_{\pi,D}$ of the donor, charge-quadrupole interactions along the π - π -stacking direction reduce IE_D and EA_D of donor molecules within the donor phase (green arrows in Fig. 5a). This shift is smaller at the interface with C₆₀ due to the interaction with its neutral $Q_{\pi,A}$ components. The negative $Q_{\pi,D}$ influences the energies of acceptor molecules (IE_A and EA_A) close to the interface, as indicated by the UPS measurements on donor-acceptor blends in Fig. 3. Therefore, the negative $Q_{\pi,D}$ induces an electrostatic potential gradient from the donor to the acceptor phase, which directly reduces ΔE_{diss} .

To analyse ΔE_{diss} in ZnPc:F₄ZnPc:C₆₀ solar cells, we obtain the difference between IE_D and EA_A in ternary blends with UPS and take this as an estimate for E_{CS} ⁴⁵. The results in Fig. 5b show that E_{CS} increases more strongly with $Q_{\pi,D}$ as compared to E_{CT} , indicating a rise of ΔE_{diss} from high ZnPc to high F₄ZnPc contents and verifying our considerations that

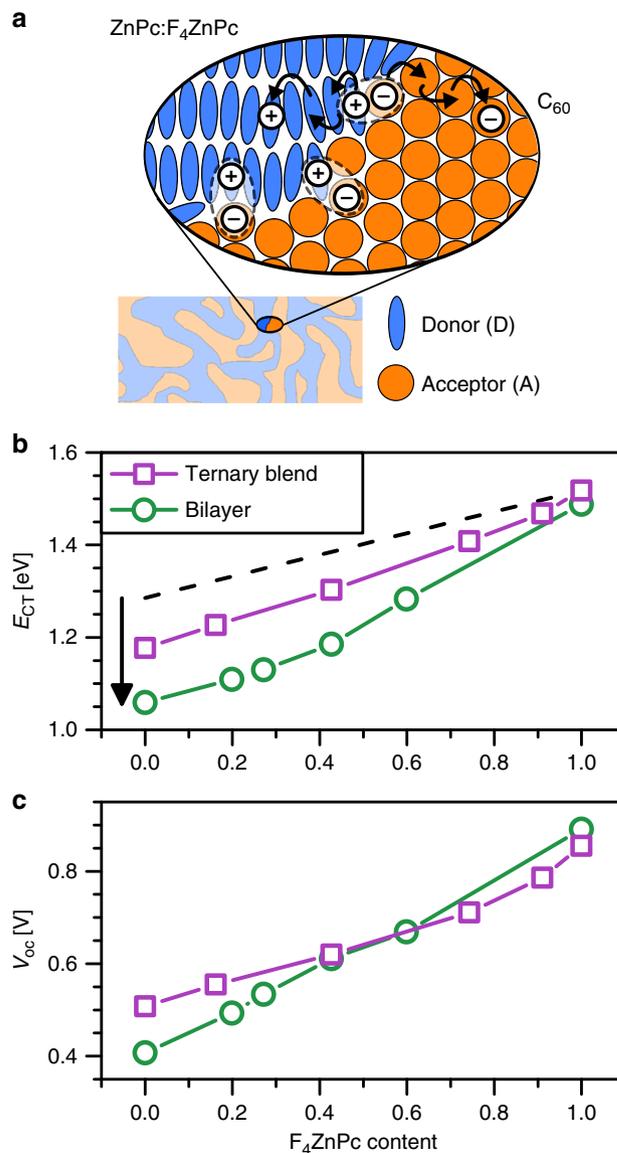


Fig. 4 Charge-transfer state energies at bulk and planar heterojunctions: **a** Simplified sketch of the interface between donor and acceptor phase in a bulk heterojunction (BHJ). The black arrows sketch a representative dissociation process of a charge-transfer (CT) exciton. **b** Experimental change of E_{CT} as a function of the molar content of F₄ZnPc in the intermixed donor phase (ZnPc:F₄ZnPc), forming a ternary BHJ (purple squares) or a planar heterojunction (green circles) with the acceptor C₆₀. E_{CT} values for the solar cells are obtained from Gaussian fits to sensitively measured external quantum efficiency (see Supplementary Fig. 11) and electroluminescence spectra⁴⁴. The dashed black line is the shift of E_{CT} , as calculated from the change of molecular parameters (see Eq. 4 in the Methods section). The black arrow highlights the decrease of E_{CT} at large ZnPc contents, which we attribute to charge-quadrupole interactions. **c** Change of V_{oc} , measured at 1 sun illumination intensity, as a function of F₄ZnPc content for both solar cell architectures. Note that the voltage losses ($\Delta V_{oc} = E_{CT}/e - V_{oc}$) are slightly lower for planar heterojunctions due to the reduced interfacial area⁵⁸

charge-quadrupole interactions can reduce ΔE_{diss} . For PHJs, we observe a similar increase of ΔE_{diss} for higher F₄ZnPc contents (Supplementary Fig. 13). We perform TDCF measurements¹¹ on ternary solar cells to investigate how the increase of ΔE_{diss} affects the generation efficiency of free charge carriers. In this

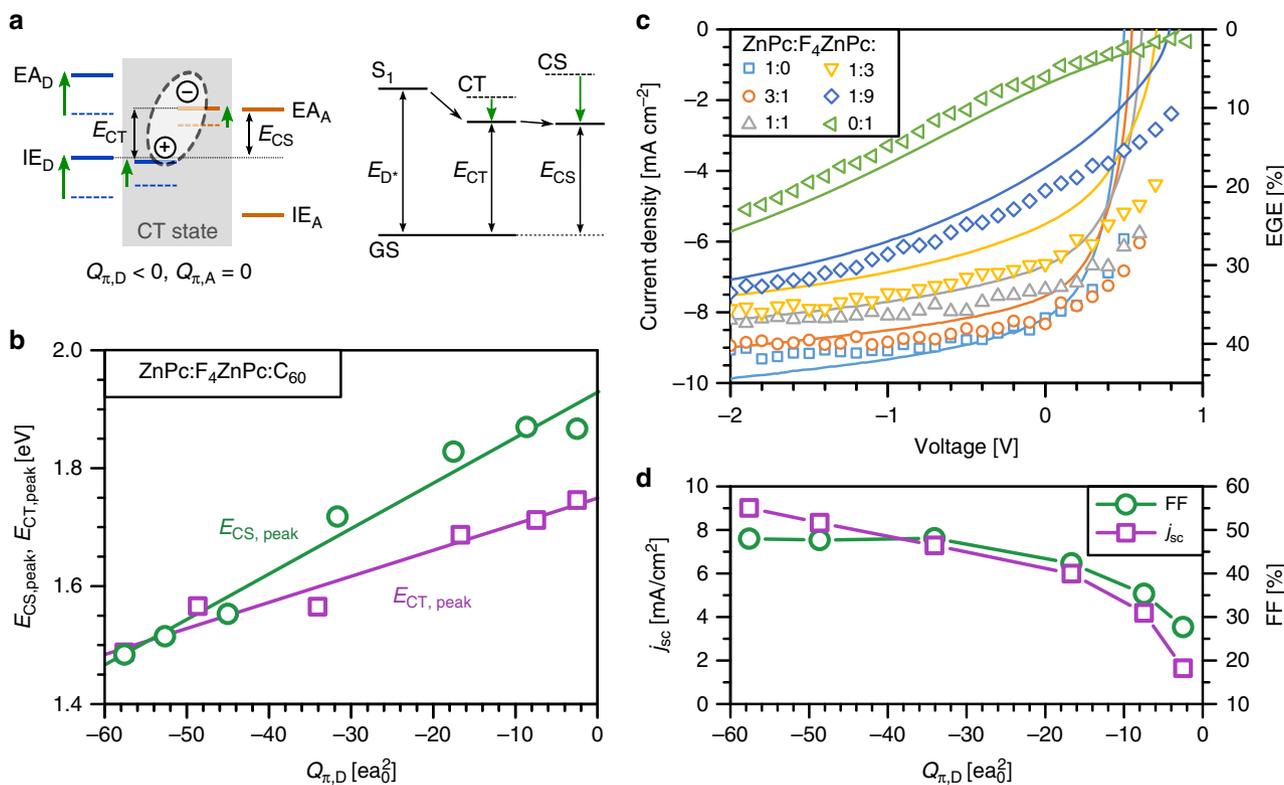


Fig. 5 CT exciton dissociation facilitated by quadrupole moments: **a** Simplified sketch of the donor and acceptor energy levels at the interface (CT state), highlighted by the grey area, and in the bulk of donor and acceptor phase for $Q_{\pi,D} = 0$ (dashed lines) and $Q_{\pi,D} < 0$ (solid lines). The green arrows illustrate the energy shifts due to charge–quadrupole interactions, reducing the CT dissociation barrier (ΔE_{diss}), i.e. the difference between the energy of separated charges (E_{CS}) and E_{CT} . The right panel sketches the change of E_{CT} and E_{CS} together with the singlet state (S_1) energy and the ground state (GS). **b** $E_{\text{CS,peak}}$, $E_{\text{CT,peak}}$ estimated from UPS measurements, increases stronger with the averaged $Q_{\pi,D}$ as compared to the peak energy of the CT state ($E_{\text{CT,peak}}$), indicating an enhancement of ΔE_{diss} with increasing $Q_{\pi,D}$, i.e. with larger F₄ZnPc contents. $E_{\text{CS,peak}}$ and $E_{\text{CT,peak}}$ are obtained from peak positions to exclude energetic disorder and experimental broadening from the analysis. Furthermore, $E_{\text{CS,peak}}$ is reduced by 0.6 eV to account for the polarisation difference between surface and bulk^{59,60}. The solid lines are guides to the eye. **c** Time-delayed collection field (TDCF) measurements show that the reduction in photocurrent and fill factor (FF) for large F₄ZnPc contents is caused by field-dependent photocurrent generation. The solid lines and left axis show the current-density/voltage characteristics of the solar cells, whereas the symbols and right axis depict the external generation efficiency (EGE) of the photocurrent. **d** The increase of ΔE_{diss} with $Q_{\pi,D}$, as shown in (b), causes a reduction of the short-circuit current density (j_{sc}) and FF of the respective solar cells measured at 1 sun illumination conditions

method, donor molecules are excited by a short laser pulse. After a delay of 8 ns, when all geminate recombination has taken place^{46,47} (Supplementary Fig. 14), the charges are extracted by applying a large negative bias voltage. As shown in Fig. 5c, the amount of collected charges follows the current-density/voltage characteristics of the solar cells, revealing that the reduced photocurrent at high F₄ZnPc contents is predominantly due to a field-dependent free charge carrier generation¹¹. We attribute the increased field-dependence to the increased ΔE_{diss} . The increase of ΔE_{diss} with $Q_{\pi,D}$ causes a significant reduction of the device parameters FF and j_{sc} once $Q_{\pi,D}$ is larger than $-30 ea_0^2$ (Fig. 5d). This finding explains the observation in previous studies where the use of F₄*ZnPc (a variant of F₄ZnPc, see Fig. 1 for the chemical structure) as donor in combination with C₆₀ yields well-performing solar cells⁴⁸. In contrast to F₄ZnPc, F₄*ZnPc has a more negative $Q_{\pi,D}$ of $-41.6 ea_0^2$, being sufficiently low to ensure efficient CT exciton separation.

The correlation of FF and j_{sc} with Q_{π} is not restricted to this particular system. We further calculate $Q_{\pi,D}$ and $Q_{\pi,A}$ values for three donors (SubNc, ZnPc, F₄*ZnPc) each combined with one non-fullerene acceptor (Cl₄SubPc or Cl₆SubPc). In PHJ devices⁴⁹, FF and j_{sc} increase for all donors when the acceptor Cl₄SubPc is substituted by Cl₆SubPc, which can be explained by the increased

difference between $Q_{\pi,D}$ and $Q_{\pi,A}$ (Supplementary Fig. 15). These results indicate that a precise adjustment of $Q_{\pi,A}$ being larger than $Q_{\pi,D}$ should be considered when designing efficient non-fullerene acceptor molecules. For example, $Q_{\pi,A}$ can be increased by adding electron withdrawing side groups to the acceptor. In literature, there are already examples of efficient acceptors having such side groups^{50,51}, where a larger degree of fluorination resulted in an improved charge extraction⁵². Furthermore, the results of a recent study indicate that quadrupole moments also affect polymer solar cells. Here, an improved charge generation in P3HT/PCBM bilayer solar cells was observed when P3HT was oriented end-on⁴², which can be explained by the reduced relevance of the positive quadrupole component along the polymer chain (see quadrupole components of alpha-6T in Supplementary Table 1 for comparison). Therefore, quadrupole moments and molecular orientation should be taken more into account for the design of future photovoltaic materials such as small molecules, oligomers and polymers.

Discussion

In conclusion, we show that charge–quadrupole interactions along the π - π -stacking direction can induce large electrostatic energy shifts to the electronic levels of molecular films, depending

on molecular orientation and blend composition. Due to the sensitivity of the interaction energy to the local morphology, the electronic levels of blends strongly depend on the mixing ratio. Utilising the example of OSCs, we show the dependency of the charge-transfer state energy at donor-acceptor interfaces on the quadrupole component in π - π -stacking direction. Moreover, we present a strategy to tune the driving force for free-charge-carrier generation by adjusting the respective quadrupole components, which can be used to optimise non-fullerene acceptor molecules. A similar correlation is found for other materials than ZnPc derivatives, suggesting that our findings can be applied to a large variety of small molecules and polymers. These results highlight the necessity to consider the quadrupole moment as an important molecular parameter in future material design for high-performing organic semiconductor devices.

Methods

Ultraviolet photoelectron spectroscopy. The spectra are acquired by a PHOIBOS 100 analyser system (Specs, Berlin, Germany) at a base pressure of 10^{-11} mbar using He I excitation lines (21.22 eV) and an energy resolution of around 150 meV. By repeating the sample production under the same experimental conditions, the experimental error for the position of the obtained energetic states is estimated to be 50 meV. The Fermi level positions of all spectra are calibrated to the Fermi edges of the gold or silver substrates. All samples are thermally (co-)evaporated at rates of 0.1 – 0.2 \AA s^{-1} in UHV at a base pressure of 10^{-8} mbar using individual quartz crystal monitors for each material. As substrates, sputter-cleaned gold foils are used for face-on orientation and silver foils covered by 5 nm of an amorphous layer of p-doped BPAPF (3 wt%, doped with NDP9) for edge-on orientation²⁹. NDP9 is a commercial p-dopant supplied by Novald GmbH, Germany. The layer thickness of the organic layers under investigation is always 20 nm. IE values are obtained from the sum of the work function and the maximum position of the HOMO peak. The work function is extracted from the onset of the high binding energy cut-off.

X-ray scattering. The experiments are performed at the ESRF, France (beamline ID03), with a photon energy of $E = 22.0$ keV. The reciprocal space maps (RSM) are measured under grazing incidence geometry with an angle of incidence of $\alpha_i = 0.07^\circ$. Each RSM is assembled from 16 single images recorded with a PILATUS 300k area detector. All measurements are performed in air. The samples are thermally (co-)evaporated at rates of 0.1 – 0.2 \AA s^{-1} in UHV at a base pressure of 10^{-8} mbar using individual quartz crystal monitors for each material. As substrates, glass substrates covered by 1 nm of chromium and 30 nm of gold are used for face-on orientation and glass substrates covered by 5 nm of an amorphous BPAPF are used for edge-on orientation²⁹. The layer thickness of the F_4 ZnPc layers is 20 nm.

Solar cell device preparation. The solar cells are thermally evaporated at ultra-high vacuum (base pressure $< 10^{-7}$ mbar) on a glass substrate with a pre-structured indium tin oxide (ITO) contact (Thin Film Devices, USA). The layer stacks of the ternary bulk heterojunction solar cells are: Glass/ITO/BPAPF:NDP9 (40 nm, 5 wt %)/ZnPc: F_4 ZnPc (5 nm, varying ratio)/ZnPc: F_4 ZnPc: C_{60} (38 nm, varying ZnPc: F_4 ZnPc ratio, 60 vol% of C_{60})/ C_{60} (15 nm)/ C_{60} :W₂(hpp)₄ (8 nm, 3 wt%)/Al (100 nm). The layer stacks for planar heterojunctions are: Glass/ITO/BPAPF:NDP9 (20 nm, 10 wt%)/ZnPc: F_4 ZnPc (10 nm, varying ratio)/ C_{60} (40 nm)/BPhen (8 nm)/Al (100 nm). NDP9 is a commercial p-dopant supplied by Novald GmbH, Germany. All the organic materials were purified 2–3 times by sublimation. The device area of 6.44 mm^2 is defined by the geometrical overlap of the bottom and the top contact, verified with a profilometer. To avoid exposure to ambient conditions, the organic part of the device is covered by a small glass substrate which is glued on top. The relative content of donor and acceptor phases in ternary blends is estimated to have a precision of better than ± 5 wt%.

Current–voltage characteristics. The current–voltage characteristics in dark and under solar illumination are measured with a source measure unit (Keithley 2400, USA) at room temperature. For the latter condition, the solar cells are illuminated with a spectrally mismatch-corrected intensity of 100 mW cm^{-2} (AM1.5G) provided by a sun simulator (16 S-150 V.3 Solar Light Co., USA) and masked to avoid edge effects and to precisely define the area. The intensity is monitored with a calibrated Hamamatsu S1337 silicon photodiode.

Sensitive external quantum efficiency (sEQE). The light of a quartz halogen lamp (50 W) is chopped at 141 Hz and coupled into a monochromator (Newport Cornerstone 260 1/4m, USA). The resulting monochromatic light is focused onto the solar cell, of which the short-circuit current is fed to a current pre-amplifier before it is analysed with a lock-in amplifier (Signal Recovery 7280 DSP, USA). The time constant of the lock-in amplifier was chosen to be 0.5 s or 1.0 s and the amplification of the pre-amplifier was increased to resolve low photocurrents.

The EQE is determined by dividing the photocurrent of the OSC by the flux of incoming photons, which was measured using a calibrated Si and InGaAs photodiode. The measurements are performed at room temperature.

Electroluminescence (EL). EL measurements were obtained at room temperature with an Andor SR393i-B spectrometer equipped with a cooled Si and cooled InGaAs CCD detector array (DU420A-BR-DD and DU491A-1.7, UK). The spectral response of the setup was calibrated with a reference lamp (Oriel 63355). The emission spectrum of the OSCs was recorded at different injection currents with respect to voltages, which were lower than or at least similar to the V_{oc} of the device at 1 sun illumination.

Time-delayed collection field. In TDCF measurements, the device is excited while held at a varying pre-bias and after a delay time of 8 ns a collection bias of 2.5 V is applied. The excitation was generated with a diode-pumped, Q-switched Nd:YAG laser (NT242, EKSPILA, 500 Hz rep-rate, 5.2 ns pulse duration, 590 nm wave-length). Also, to compensate for the internal latency of the pulse generator, the laser pulse was delayed and homogeneously scattered in an 85 m long silica fibre (LEONI). An Agilent 81150A pulse generator was employed to apply the pre-bias and collection bias to a homebuilt amplifier directly connected to the sample. The current through the device was measured via a grounded 10 \Omega resistor in series with the sample and recorded with an Agilent DSO9104H oscilloscope.

Density functional theory. The simulations are performed to calculate the molecular quadrupole moments, the ionisation energy, and the intramolecular relaxation energy in gas-phase of the relevant molecules. The quadrupole tensor components Q_{ij} are obtained from following definition:

$$Q_{ij} = \int p(\mathbf{r}) \cdot (3r_i r_j - |\mathbf{r}|^2 \delta_{ij}) \cdot d^3 \mathbf{r}. \quad (2)$$

The ionisation energy was determined as the difference of the total energy of the positively charged molecule and the neutral molecule in the relaxed geometry of the neutral molecule. The intramolecular relaxation energy is determined as the difference in total energy between the negatively (positively) charged molecule in its optimised geometry and its energy in the geometry of the neutral molecule. We used the M06-2x exchange-correlation functional⁵³ and the correlation-consistent basis set cc-pVTZ⁵⁴ as implemented in the computational chemistry package NWChem⁵⁵.

Charge–quadrupole interaction energy calculation. The energy is calculated for a given molecule at site \mathbf{r}_j as a discrete sum including all other molecules (at sites \mathbf{r}_i) in the considered geometry, according to

$$E_Q(\mathbf{r}_j) = \sum_{i,k} \frac{q_{j,k}}{8\pi\epsilon_0\epsilon_r} \frac{(\mathbf{r}_i - \mathbf{r}_j - \boldsymbol{\tau}_k) \cdot \mathbf{Q}_i \cdot (\mathbf{r}_i - \mathbf{r}_j - \boldsymbol{\tau}_k)}{|\mathbf{r}_i - \mathbf{r}_j - \boldsymbol{\tau}_k|^5} \quad (3)$$

with the quadrupole tensor \mathbf{Q}_i of molecule i and the relative dielectric permittivity (assuming $\epsilon_r = 2.8$ ⁵⁶ for all F_4 ZnPcs). Hereby, $q_{j,k}$ is the fractional excess charge at atom k of the molecule j and $\mathbf{r}_j + \boldsymbol{\tau}_k$ is its position. The quadrupole tensor and the fractional excess charges are obtained in gas phase for all molecules in their respective relaxed structures. The charge distributions and the resulting quadrupole moments might slightly differ in the film phase due to the surrounding polarisable medium. The film structure was generated according to the crystal structure of CuPc⁵⁷ (see Supplementary Figs. 1–4). We assume a simplified orthorhombic lattice and take the intermolecular distances (approximately constant 3.8 Å and 13.5 Å) from literature^{28,30}. For face-on geometry, a film thickness of 20 nm implies that we take into account 53 layers along the surface normal. We restrict the summation in lateral directions to a large area of $400 \text{ nm} \times 400 \text{ nm}$, which is sufficient for convergence. For edge-on geometry, we have 15 layers in the direction of the surface normal for a 20 nm film, while the lateral dimension of the integration region is equally big. To investigate the relevant range for the interaction energy, we vary the summation in lateral direction between 10 and 200 nm (Supplementary Fig. 5). In addition, we reduced the thickness of the film in edge-on orientation from 20 to 3 nm and observe an increase of the interaction energy by 10% for ZnPc, in good agreement to the change of IE observed in experiment (Fig. 2d).

Energy change of CT states due to molecular parameters. We estimate the variation of the CT state energy (E_{CT}) from the change of molecular parameters when replacing ZnPc with F_4 ZnPc using following expression:

$$E_{CT} = IE_{0,D} - EA_{0,A} - E_{\text{coul},CT} - \lambda_D - \lambda_A, \quad (4)$$

where $IE_{0,D}$ is the gas-phase ionisation energy of the donor (ZnPc/ F_4 ZnPc) and $EA_{0,A}$ is the gas-phase electron affinity of the acceptor (C_{60}). $E_{\text{coul},CT}$ is the Coulomb binding energy between the donor cation and the acceptor anion, which is screened by a mean dielectric constant of $\epsilon_r = 3.6$, obtained from $\epsilon_r = 2.8$ for ZnPc and $\epsilon_r = 2.8$ for C_{60} ⁵⁶. For a detailed description how $E_{\text{coul},CT}$ is obtained, we refer the reader to our previous publication⁴³. λ_D is the intramolecular relaxation energy of the donor cation and λ_A is the intramolecular relaxation energy of the

acceptor anion. All values are obtained from DFT simulations. To compare with the experimental data in Fig. 4b, we additionally subtract a polarisation energy of 2.1 eV.

Data availability

All the data supporting the findings of this study are available within the article, its Supplementary Information files, or from the corresponding authors upon reasonable request.

Code availability

The code used for the calculation of the charge–quadrupole interaction energy is available from the corresponding authors upon reasonable request.

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Author contributions

M.S. designed the study and acquired most of the UPS data. K.S.S., C.G. and R.S. performed DFT simulations. K.O. acquired further UPS data. F.O. calculated charge–quadrupole interaction energies. A.H. performed X-ray scattering experiments. J.B., M.S. and K.V. designed the solar cell devices and J.B. did the characterisation. J.B. and J.K. performed sensitive EQE measurements, whereas J.B. evaluated the data. L.P.T. performed TDCF and EL measurements on ternary BHJ solar cells. S.R. performed EL measurements on PHJ solar cells. M.L. synthesised F₈ZnPc. K.L., F.O., K.V., G.C., F.S. and D.N. supervised different parts of the study. D.A. and C.P. valuably contributed to the physical understanding of the underlying electrostatic interactions. M.S., F.O. and K.L. wrote the manuscript and all authors contributed to discussions and finalising the manuscript.

Additional information

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